the heat of formation of MnSe to -37.8 kcal/mole. Because of the error limits of the various quantities involved in these calculations, a preference of one of the dissociation energies on the basis of these measurements is not justified.

The calculational technique used for the evaluation of the MnSe Knudsen data was applied to the MnS system which vaporizes predominantly according to Reaction (1). Under the experimental conditions of the MnS vaporization[33] and with $D_0°(S_2)=101$ kcal/mole, the degree of dissociation of sulfur is calculated with Eq. (17) to be 0.06. This is in good agreement with mass spectrometric results.[7]

It will be the purpose of Langmuir-type measurements to reveal the mechanism of vaporization in these systems.

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Quantum-Mechanical Treatment of Inelastic Collisions. I. General Theory and Application to Nonreactive Collisions

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A general method for the quantum-mechanical treatment of the inelastic collision of composite particles is presented. The method, which is applicable to both nonreactive and reactive collisions, consists of constructing the total stationary scattering wavefunction describing the collision as a linear combination of linearly independent functions which satisfy the Schödinger equation and also arbitrary boundary conditions specified in the asymptotic region. The formalism is developed for nonreactive collisions using a collinear model to simplify the mathematical treatment. In this paper, it is applied to two examples of impulsive collisions. In one case, for which a comparison is possible, calculated transition probabilities agree well with previously published values.

I. INTRODUCTION

There exists a large volume of literature devoted to the theoretical study of energy transfer in the inelastic collision of composite particles. In particular, the problem of energy transfer between translational and vibrational and rotational degrees of freedom has received a great deal of attention. Takayanagi[1] has written two excellent review of the work done in this field.

A great proportion of the theoretical work has been done on collinear (one-dimensional) models representing the collision between an atom and a diatomic molecule or a solid surface or between two diatomic molecules. Although this restricted treatment cannot give a quantitative explanation of experimental data, it can show us qualitatively, or semiquantitatively, some characteristic features of the problem and also gives us a convenient basis from which to proceed to more general treatments. It may also be argued reasonably that the configuration allowing the most efficient transfer of energy is that in which the molecule and atom are collinear.

The model of a diatomic molecule, represented by a harmonic oscillator, being struck by an atom (free particle) has been treated classically,[2,3] semiclassically,[4] and quantum mechanically by the method of distorted waves.[5,6] Schuler and Zwanzig[7] have calculated numerically the quantum-mechanical transition probabilities for the impulsive collision (collinear) of a free particle with a particle oscillating harmonically about a fixed equilibrium position, a problem mathematically equivalent to the atom–diatomic collision. Their method consists of expanding the total stationary scattering solution $\Psi(R, r)$ as a linear combination of products of the bound-state eigenfunctions of the oscillator and free-particle wavefunctions such that

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† Contribution No. 3596.

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Ψ satisfies the Schrödinger equation describing the collision. Shuler and Zwanzig satisfied the impulsive condition $[\Psi(R, r=R)=0]$ in a least-squares sense by expanding $\Psi(R, R)$ in the complete orthonormal set of harmonic-oscillator eigenfunctions. This results in a set of simultaneous equations. The matrix corresponding to this set of equations is inherently ill conditioned, but Shuler and Zwanzig found that they could obtain transition probabilities which had converged to several significant figures by using successively larger matrices. We have attempted to apply this method to the impulsive collision between *two* diatomic molecules. However, the number of equations in the truncated set increases as the *square* of the number of channels retained in the state expansion so that numerical instability sets in before the probabilities converge.

The Shuler–Zwanzig method has the clear disadvantage (in addition to numerical instability) that it is applicable only to impulsive collisions. Secrest and Johnson[8,9] have recently developed a general method of treating inelastic collisions. They call their formalism the method of "amplitude density functions." It consists of breaking the complete scattering problem up into several problems involving weaker interaction potentials and "adding" up the solutions of these individual problems to obtain the total solution. Secrest and Johnson[8] have applied their procedure to the atom–diatomic collision problem using a range of interaction potentials from very "soft" to very "hard." In particular, they were able to duplicate the results of Schuler and Zwanzig by approximating the hard-sphere interaction by a step potential +25 oscillator units high.

The principal purpose of this paper is to develop a new general method for treating the problem of energy transfer occurring in the inelastic collision of composite particles. Essentially the theory consists of constructing the total scattering wavefunction as a linear combination of members of a set of linearly independent solutions of the relevant Schrödinger equation, each solution of the set satisfying a *distinct*, yet *arbitrary*, boundary condition specified in the asymptotic region. It will be shown that the method is capable of handling both *nonreactive* (e.g., vibrational excitation) and *reactive* (i.e., exchange reactions) collisions. In order to keep the discussion clear and simple we shall first present the formalism for nonreactive, collinear collisions. We shall then consider several specific examples which demonstrate the utility of the method. In a future publication[10] the theory will be extended to treat exchange reactions of the type A+BC→AB+C.

In Sec. II we develop the general theory for vibrational excitations, using the atom–diatomic collision as an example. The determination of the set of linearly independent solutions, χ_j's, by the method of finite differences is the subject of Sec. III, in which we also consider the analysis of the χ_j's into their separable components in the asymptotic region and also the convergence of the χ_j's and the transition probabilities as a function of the mesh size. In Sec. IV, we apply the theory to two problems in vibrational excitation. Finally, we discuss the results and possible further applications of the theory in Sec. V.

II. GENERAL THEORY

To clarify the presentation of the theory, we shall consider the *collinear* atom–diatomic collision which is depicted in Fig. 1. Letting m_1, m_2, m_3 and x_1, x_2, x_3 denote the masses and coordinates of the three particles, respectively, we may write the time-independent Schrödinger equation describing the collision as

$$\left\{-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2}-\frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2}-\frac{\hbar^2}{2m_3}\frac{\partial^2}{\partial x_3^2}+V_{12}'[(x_1-x_2)]+V_I'[(x_2-x_3)]\right\}\Psi=E\Psi, \quad (1)$$

where we have assumed that particles 1 and 2 (diatomic) are bound by the potential V_{12}' and that the incident particle (atom) 3 interacts only with particle 2 of the bound pair. E is the total energy.

In the center-of-mass coordinate system, defined by the following transformation:

$$X=(m_1x_1+m_2x_2+m_3x_3)/M \quad (2a)$$

$$x'=x_3-(m_1x_1+m_2x_2)/m \quad (2b)$$

$$y'=x_2-x_1, \quad (2c)$$

where $M=m_1+m_2+m_3$ and $m=m_1+m_2$, the Schrödinger equation (1) becomes

$$\left\{-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2}-\frac{\hbar^2}{2\mu_{12,3}}\frac{\partial^2}{\partial x'^2}-\frac{\hbar^2}{2\mu_{12}}\frac{\partial^2}{\partial y'^2}+V_{12}'(y')+V_I'\left(x'-\frac{m_1}{m}y'\right)\right\}\Psi=E\Psi, \quad (3)$$

where $\mu_{12,3}=mm_3/M$ and $\mu_{12}=m_1m_2/m$.

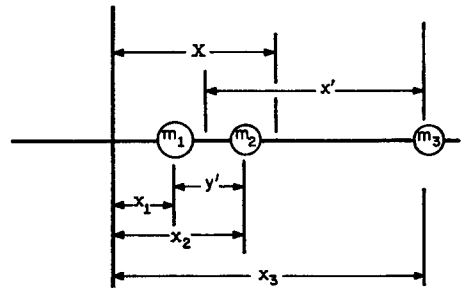

FIG. 1. Diagram of the collinear collision of an atom (m_3) with a diatomic molecule (m_1–m_2) showing relation between coordinate systems.

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[9] B. Johnson and D. Secrest, J. Math. Phys. **7**, 2187 (1966).
[10] D. J. Diestler and Vicent McKoy, J. Chem. Phys. **48**, 2951 (1968).

Since the potential energy does not depend on the center-of-mass coordinate, X, we can separate variables in Eq. (3) by making the substitution $\Psi=\Phi_{\text{c.m.}}(X)\chi(x', y')$. The equation for the relative motion is then found to be

$$\left\{-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}-\frac{\hbar^2}{2\mu_{12}}\frac{\partial^2}{\partial y^2}+V_{12}(y)+V_I(x-y)\right\}\chi=E_r\chi, \quad (4)$$

where

$$x'=(x+y_0)m_1/m,$$
$$y'=(y+y_0),$$
$$\mu=m_3m_1^2/mM,$$
$$V_{12}(y)=V_{12}'(y'-y_0),$$
$$V_I(x-y)=V_I'[(m_1/m)(x-y)],$$
$$E=E_{\text{c.m.}}+E_r,$$

and y_0 is the equilibrium separation of 1 and 2. We see from Eq. (4) that our problem is mathematically equivalent to that of a particle of mass μ_{12} oscillating about an equilibrium position being struck by a particle of mass μ. We can simplify the treatment by adopting this point of view.

In Fig. 2(a) is drawn a schematic diagram of the collision described by the Schrödinger equation (4). We assume that the bound particle (μ_{12}) has a discrete eigenvalue spectrum and is bound tightly enough that $\chi(x, y)=0$ for $|y|\geq a$. Furthermore, we assume that the range of the interaction potential is such that $V_I=0$ if $x\geq x_0$, $x\leq x_0'$ when transmission is allowed. When no transmission is allowed, the interaction potential becomes infinite for $x\leq x_0'$. The "cutoffs" x_0 and x_0' thus specify the extent of what we shall refer to as the *inseparable* (interaction) region [see Fig. 2(b)]. Outside the interaction region, where the Schrödinger equation is separable, we seek a total scattering wavefunction of the form

$$\chi=\exp(-ik_Ix)\phi_I(y)+\sum_{m=1}^{N}R_m\exp(ik_mx)\phi_m(y)+\mathcal{O}(e^{-\lambda x}), \quad x\gtrsim x_0 \quad (5a)$$

$$\chi=\sum_{m=1}^{N}T_m\exp(-ik_mx)\phi_m(y)+\mathcal{O}(e^{\lambda x}), \quad x\leq x_0', \quad (5b)$$

where the ϕ_m are eigenfunctions of the bound particle which satisfy

$$-(\hbar^2/2\mu_{12})(\partial^2\phi_m/\partial y^2)+V_{12}(y)\phi_m=\epsilon_m\phi_m, \quad (6)$$

and the exponential factors are the corresponding free-particle wavefunctions. Since the total energy is conserved, we must have

$$\epsilon_m+(\hbar^2k_m^2/2\mu)=E_r. \quad (7)$$

From Eqs. (5) we see that there are N open channels, i.e., the incoming particle has sufficient energy to excite the bound particle to any of its lowest N eigenstates. In the asymptotic region $x\geq x_0$ the total scattering wavefunction χ consists of an incoming wave of unit amplitude in channel I plus reflected waves of amplitudes R_m in the various open channels, m. In the other asymptotic region ($x\leq x_0'$) χ, Eq. (5b), consists of transmitted waves of amplitude R_m in the various open channels. The terms $\mathcal{O}(e^{-\lambda x})$ in Eq. (5a) and $\mathcal{O}(e^{\lambda x})$ in Eq. (5b) indicate contributions to χ from *virtual* (energetically inaccessible) states, which are included for mathematical completeness as we shall see below. Physically, Eq. (5a) describes a free particle of momentum $\hbar k_I$ impinging on a particle bound initially in state I, exciting (or de-exciting) the bound particle to state m with a probability given by

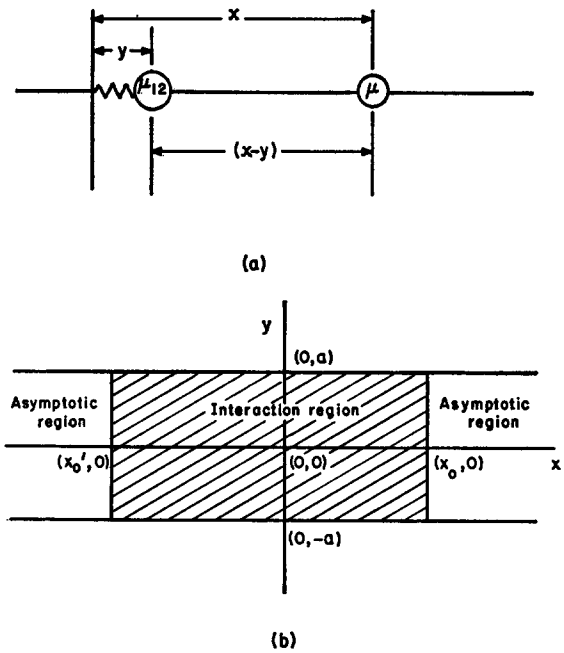

FIG. 2. (a) Diagram of a collision of a free particle with a particle bound to a fixed center of force. (b) Boundary conditions and interaction (inseparable) region for collision diagrammed in (a).

$$P_{I\to m}^{(R)}=(k_m/k_I)\,|\,R_m\,|^2, \quad (8a)$$

and finally reflecting back in the direction $(+x)$ from which it came. Equation (5b) corresponds to the incident particle's exciting (or de-exciting) the bound particle to state m with probability

$$P_{I\to m}^{(T)}=(k_m/k_I)\,|\,T_m\,|^2, \quad (8b)$$

and continuing on its path in the same direction $(-x)$. Relations (8a) and (8b) are obtained by identifying the transition probability $P_{I\to m}$ with the ratio of current scattered into channel m to the incident current $\hbar k_I/m$ in channel I.

Conservation of current requires that

$$\sum_{m=1}^{N}\frac{k_m}{k_I}\,|\,R_m\,|^2+\sum_{m=1}^{N}\frac{k_m}{k_I}\,|\,T_m\,|^2=1, \quad (9)$$

an equation which serves as a useful check on numerical calculation of the transition probabilities. Another check is provided by time-reversal invariance. In quantum scattering processes this invariance requires that $P_{i\to j}=P_{j\to i}$, i.e., the probability of a transition from state i to state j is equal to that of a transition from state j to i.[11] We now turn to the central problem—determination of R_m and T_m.

The crux of the method is to find a set of linearly independent solutions χ_j of the Schrödinger equation, each solution of the set satisfying a *distinct arbitrary* boundary condition specified in the asymptotic regions $x\leq x_0'$, $x\geq x_0$. For example, we may set $\chi_j(x_0', y)=\phi_j(y)$, $\chi_j(x_0, y)=\phi_{j+1}(y)$. These conditions, along with those that $\chi_j(x, \mid y\mid >a)=0$, are sufficient to determine a unique solution of Schrödinger's equation. The various χ_j corresponding to the different boundary conditions (labelled by j) are rigorously linearly independent, since the boundary conditions are specified to be linearly independent. This point will be discussed in greater detail below. Although none of the solutions χ_j will have the correct asymptotic form, each may be expressed in the regions $x\leq x_0'$, $x\geq x_0$, as

$$\chi_j(x,y)=\sum_{l=1}^{N}[A_l^{(j)}\exp(-i\mid k_l\mid x)+\bar{A}_l^{(j)}\exp(i\mid k_l\mid x)]\phi_l(y)+\sum_{l>N}[B_l^{(j)}\exp(-\mid k_l\mid x)+\bar{B}_l^{(j)}\exp(\mid k_l\mid x)]\phi_l(y), \quad (10a)$$

$$\chi_j(x,y)=\sum_{l=1}[\alpha_l^{(j)}\exp(-i\mid k_l\mid x)+\bar{\alpha}_l^{(j)}\exp(i\mid k_l\mid x)]\phi_l(y)+\sum_{l>N}[\beta_l^{(j)}\exp(-\mid k_l\mid x)+\bar{\beta}_l^{(j)}\exp(\mid k_l\mid x)]\phi_l(y), \quad (10b)$$

respectively, where

$$(\hbar^2k_l^2/2\mu)+\epsilon_l=E_T. \quad (11)$$

We note that χ_j satisfies the wave equation, Eq. (4). The first sum in each of Eqs. (10) is over open channels. The corresponding k_l in Eq. (11) are pure real for $l\leq N$. The second sum is over all virtual channels, for which k_l is pure imaginary in Eq. (11). We may regard χ_j as being expanded in a subset of the complete orthonormal set of eigenfunctions of the Hamiltonian $H-V_I$. This subset is *not* complete in the mathematical sense that an arbitrary well-behaved function can be expanded in terms of it. However, any function χ satisfying Eq. (4) may be expanded as in Eqs. (10). We shall see below that any physically acceptable χ may be expressed as a linear combination of open and *decaying* virtual-channel functions.

Now the total scattering solution ψ is constructed as a linear combination of the linearly independent χ_j as

$$\psi=\sum_{j=1}^{\infty}c_j^{(I)}\chi_j, \quad (12)$$

such that ψ is everywhere a solution of Eq. (4) and also satisfies the correct asymptotic conditions [Eq. (5)]. We shall refer to the right member of Eq. (12) as the *state expansion* of ψ. Thus we must require

$$\sum_j c_j^{(I)}A_l^{(j)}=\delta_{Il}, \qquad l\leq N, \quad (13a)$$

$$\sum_j c_j^{(I)}\bar{B}_l^{(j)}=0, \qquad l>N, \quad (13b)$$

$$\sum_j c_j^{(I)}\bar{\alpha}_l^{(j)}=0, \qquad l\leq N, \quad (13c)$$

$$\sum_j c_j^{(I)}\beta_l^{(j)}=0, \qquad l>N, \quad (13d)$$

where the superscript (I) on the $c_j^{(I)}$ denotes the incident state. Physically, Eq. (13a) states that there is only a single incoming wave incident from the right in channel I and Eq. (13c) states that there are no incident waves from the left. Equations (13b) and (13d) require that there be no *rising* virtual components in either asymptotic region.

In practice we anticipate solving Eqs. (13) by truncating the state expansion in the index j and the asymptotic expansion of χ_j in the index l to obtain a finite system of simultaneous linear equations. Suppose we retain a total of M channels, N open and $M-N$ virtual, in the l expansion in Eqs. (10). Then there are $2M$ Eqs. (13) so that we must determine $2M$ linearly independent χ_j's. If this is done Eqs. (13) may be expressed more compactly in matrix form as

$$\mathbf{AC}=\mathbf{I}', \quad (14)$$

where $\mathbf{A}$ is a $2M\times 2M$ matrix of coefficients $A_l^{(j)}$, $\bar{B}_l^{(j)}$, etc., $\mathbf{C}$ is a $2M\times N$ matrix of unknown coefficients $c_j^{(I)}$, and $\mathbf{I}'$ is a $2M\times N$ matrix consisting of a $N\times N$ unit matrix spanning the first N rows and a $(2M-N)\times N$ null matrix spanning the remaining. The column vectors of $\mathbf{C}$ correspond to the various possible incident states $I=1, 2, 3\cdots N$. Having obtained $\mathbf{C}$ by solving Eq. (14), we can find the reflection and transmission coefficient by taking the product

$$\mathbf{AC}=\mathbf{AA}^{-1}\mathbf{I}', \quad (15)$$

where $\mathbf{A}$ is a $N\times 2M$ matrix of coefficients $\bar{A}_l^{(j)}$ and $\alpha_l^{(j)}$ corresponding to the equations

$$\sum_j c_j^{(I)}\bar{A}_l^{(j)}=R_l^{(I)}, \qquad l\leq N, \quad (16a)$$

$$\sum_j c_j^{(I)}\alpha_l^{(j)}=T_l^{(I)}, \qquad l\leq N. \quad (16b)$$

III. DETERMINATION OF χ_j

Having developed the formalism of the method, we now turn to the central problem: determination of the

[11] A. Messiah, *Quantum Mechanics* (North-Holland Publ. Co Amsterdam, 1965), Vol. 2, p. 806.

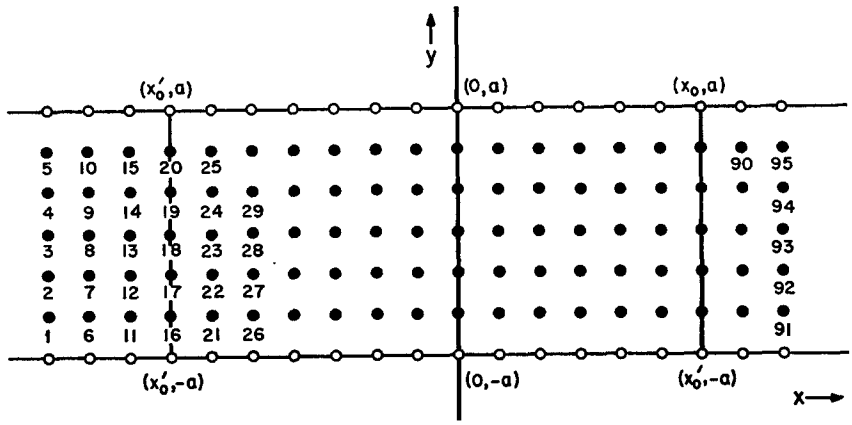

FIG. 3. Finite-difference mesh used in the solution of the atom–diatomic collision problem.

linearly independent solutions χ_j. Our task is to solve a second-order elliptic partial differential equation with Dirichlet boundary conditions. Since the total energy is fixed, we do not have an eigenvalue problem. For the solution of such a problem there are two generally useful techniques: (a) expansion of χ_j in a complete set of functions; (b) finite differences. In a future paper we shall discuss the application of technique (a) to the determination of χ_j. However, for the examples to be considered in the present paper we have employed the method of finite differences. Hence, we have only to find the solution (discretized χ_j) of the set of simultaneous linear equations resulting from the discretization of the Schrödinger equation for a fixed energy E_r.

Substituting the appropriate expressions for the discretized partial derivatives,[12] we obtain for the five-point finite-difference (three points in each dimension) analog of the wave equation Eq. (4)

$$[2(\mu^{-1}+\mu_{12}^{-1})+2h^2(V_{12}'+V_I'-E_r')_i]\chi_i-\mu^{-1}(\chi_{i_1}+\chi_{i_3})-\mu_{12}^{-1}(\chi_{i_2}+\chi_{i_4})=0, \qquad i=1, 2, 3\cdots Q, \quad (17)$$

where i labels the interior mesh points which are numbered as shown in Fig. 3 and h is the mesh size. The mesh points immediately surrounding i are labelled i_1, i_2, i_3, i_4 counterclockwise beginning with the extreme right-hand point. In Eq. (17) we note that $\hbar^2$ has been absorbed into V_{12}, V_I, and E_r and also that the subscript j on χ_j has been suppressed. The set of equations [Eq. (17)] may be rewritten in matrix form as

$$\mathbf{H}\chi=\mathbf{b}. \quad (18)$$

$\mathbf{H}$ is a *real symmetric band* matrix of order Q (the number of interior mesh points). The bandwidth, defined by the expression bandwidth$=2B-1$, where $H_{ij}=0$ if $|i-j|\geq B$, is determined by the number of points "across the well" (i.e., the number of points which divide the range of the variable y in the finite-difference mesh), n_w. χ is the column vector of approximate values of χ_j at the grid points. $\mathbf{b}$ is a column vector of the form

$$\begin{pmatrix} \chi\{x\leq x_0', [a/(n_w+1)]\}\mu^{-1} \\ \chi\{x\leq x_0', [2a/(n_w+1)]\}\mu^{-1} \\ \vdots \\ \chi\{x\leq x_0', [n_w a/(n_w+1)]\}\mu^{-1} \\ 0 \\ \vdots \\ 0 \\ \chi\{x\geq x_0, [a/(n_w+1)]\}\mu^{-1} \\ \chi\{x\geq x_0, [2a/(n_w+1)]\}\mu^{-1} \\ \vdots \\ \chi\{x\geq x_0, [n_w a/(n_w+1)]\}\mu^{-1} \end{pmatrix}.$$

The form of $\mathbf{b}$ corresponds to the nonzero boundary conditions at either end of the interaction region which occur as "off-diagonal" terms in the left member of Eq. (17).

Uniqueness and Convergence

The uniqueness of the solution of the finite-difference equations resulting from elliptic partial differential equations has been discussed elsewhere.[13] We wish to consider further the explicit dependence of the convergence of the solutions χ and the transition probabilities upon the mesh size h. We assume that there exists a continuous function $\chi_c(x, y; h)$ such that χ_c satisfies the difference equation for all values of h and that χ_c may be expanded in a power series of the form

$$\chi_c(x, y; h)=\sum_k \xi_k(x, y)h^k, \quad (19)$$

[12] See, for example, J. Todd, *Survey of Numerical Analysis* (McGraw-Hill Book Co., New York, 1962).

[13] P. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Co., New York, 1953), Vol. 1, p. 698.

where the ξ_k may in turn be expanded in *a* complete set of linearly independent functions which are the exact solutions of Eq. (4). Note that this complete set of exact functions $\{\chi_j(x, y; E_r)\}$ is labelled by two indices: j, the *discrete* index denoting the particular boundary condition which χ satisfies, and E_r, the *continuous* index specifying the energy of the function. Hence, an arbitrary function $f(x, y)$ may be expanded as

$$f(x, y) = \sum_j S_{E_r}\, a_j(E_r)\chi_j(x, y; E_r). \tag{20}$$

In the asymptotic region this expansion assumes the form

$$f(x, y) = \sum_{l=1} \int d\,|\,k\,|\,[a_l(k)\,\exp(-i\,|\,k\,|\,x) + \bar{a}_l(k)\,\exp(i\,|\,k\,|\,x)]\phi_l + \sum_{l>N} \int d\,|\,k\,|\,[b_l(k) \times \exp(-|\,k\,|\,x) + \bar{b}_l(k)\,\exp(|\,k\,|\,x)]\phi_l. \tag{21}$$

Thus, each ξ_k will have the asymptotic form Eq. (21). χ_c must satisfy the difference-equation analog

$$[2(\mu^{-1}+\mu_{12}^{-1}) + 2h^2(V_{12}'+V_I')]\chi_c(x, y; h) - \mu^{-1}\chi_c(x+h, y; h) - \mu^{-1}\chi_c(x-h, y; h) - \mu_{12}^{-1}\chi_c(x, y+h; h) - \mu_{12}^{-1}\chi_c(x, y-h; h) = \epsilon\chi_c(x, y; h), \tag{22}$$

where $\epsilon = 2h^2E_r'$. Substituting Taylor's series expansions for χ_c into Eq. (22), replacing $\chi_c(x, y; h)$ with its expansion Eq. (19), making appropriate cancellations, and equating coefficients of equal powers of h, we obtain

$$\left\{-(2\mu)^{-1}\frac{\partial^2}{\partial x^2} - (2\mu_{12})^{-1}\frac{\partial^2}{\partial y^2} + V_{12}' + V_I'\right\}\xi_0 = E_r'\xi_0, \tag{23a}$$

$$\left\{-(2\mu)^{-1}\frac{\partial^2}{\partial x^2} - (2\mu_{12})^{-1}\frac{\partial^2}{\partial y^2} + V_{12}' + V_I'\right\}\xi_1 = E_r'\xi_1, \tag{23b}$$

$$\left\{-(2\mu)^{-1}\frac{\partial^2}{\partial x^2} - (2\mu_{12})^{-1}\frac{\partial^2}{\partial y^2} + V_{12}' + V_I'\right\}\xi_2 + \left\{-(24\mu)^{-1}\frac{\partial^4}{\partial x^4} - (24\mu_{12})^{-1}\frac{\partial^4}{\partial y^4}\right\}\xi_0 = E_r'\xi_2. \tag{23c}$$

Since ξ_0 satisfies the Schrodinger equation and the boundary condition, we have that $\xi_0 \equiv \chi_j$, the exact solution of the problem. Hence, the approximate finite-difference solution may be expressed as $\chi_c = \chi_j + h\xi_1 + h^2\xi_2$ and χ_c approaches the exact solution as $\mathcal{O}(h)$ as h approaches zero. Although ξ_1 also satisfies the Schrödinger equation, it need not satisfy the boundary condition. Now the asymptotic form of χ_c may be written for $x \geq x_0$

$$\chi_c = \sum_{l=1}^{N} [(A_{l0}+A_{l1}h+A_{l2}h^2+\cdots)\,\exp(-i\,|\,k_l\,|\,x) + (\bar{A}_{l0}+\bar{A}_{l1}h+\bar{A}_{l2}h^2+\cdots)\,\exp(i\,|\,k_l\,|\,x)]\phi_l + \sum_{l>N} [(B_{l0}+B_{l1}h+B_{l2}h^2+\cdots)\,\exp(-\,|\,k_l\,|\,x) + (\bar{B}_{l0}+\bar{B}_{l1}h+\bar{B}_{l2}h^2+\cdots)\,\exp(|\,k_l\,|\,x)]\phi_l, \tag{24}$$

where the various channel coefficients have been expanded in powers of h. This is possible since the asymptotic form of each ξ_k can be expanded in the complete set of eigenfunctions of the Hamiltonian $H-V_I$ as discussed above. We note that for $k>2$, however, A_{lk}, $\bar{A}_{lk}$, B_{lk}, $\bar{B}_{lk}$ are functions of x in general. Corresponding to the expansion Eq. (24) matrix Eq. (14) becomes

$$(\mathbf{A}_0+\mathbf{A}_1h+\mathbf{A}_2h^2+\cdots)(\mathbf{C}_0+\mathbf{C}_1h+\mathbf{C}_2h^2+\cdots) = \mathbf{I}'. \tag{25}$$

Identifying coefficients of equal powers of h on either side of Eq. (25), we find

$$\mathbf{C}_0 = \mathbf{A}_0^{-1}\mathbf{I}', \tag{26a}$$

$$\mathbf{C}_1 = -\mathbf{A}_0^{-1}\mathbf{A}_1\mathbf{C}_0, \quad \text{etc.} \tag{26b}$$

From Eq. (15) we see that the matrix of approximate amplitudes is given by

$$(\bar{\mathbf{A}}_0+\bar{\mathbf{A}}_1h+\bar{\mathbf{A}}_2h^2+\cdots)(\mathbf{C}_0+\mathbf{C}_1h+\mathbf{C}_2h^2+\cdots) = \bar{\mathbf{A}}_0\mathbf{C}_0 + (\bar{\mathbf{A}}_0\mathbf{C}_1+\mathbf{A}_1\mathbf{C}_0)h+\cdots. \tag{27}$$

Thus, the approximate transition probabilities determined by the finite-difference method approach the exact values as the mesh size tends to zero.

$$P_{i\to j}(h) = (P_{i\to j})_0 + (P_{i\to j})_1h + (P_{i\to j})_2h^2+\cdots. \tag{28}$$

Equation (28) may be used to extrapolate to the exact transition probability $(P_{i\to j})_0$ using the Richardson[14] procedure. We obtain a sequence of values $P_{i\to j}(h_1)$, $P_{i\to j}(h_2)$, $P_{i\to j}(h_3)$, etc. corresponding to mesh sizes h_1, h_2, h_3, etc. in decreasing order and fit a polynomial of the form Eq. (28) through these points. Alternatively, we may regard $P_{i\to j}(h)$ as a "mathematical transient" and apply the e_1^m transform to enhance the convergence of the sequence.[15] We shall use this latter method in the examples considered below.

Solution of Finite-Difference Equations

Depending on the extent of the interaction region and on the accuracy we demand of the transition probabilities, it may be necessary to solve very large systems of simultaneous equations, Eq. (18). For the two cases considered in this paper, it is necessary to solve up to 1500 simultaneous linear equations, the corresponding

[14] L. Richardson and J. Gaunt, Trans. Roy. Soc. (London) **A226**, 299 (1927).

[15] D. Shanks, J. Math. Phys. **34**, 1 (1955).

matrix $\mathbf{H}$ having a bandwidth of 81. To accomplish this we have employed a highly accurate and efficient computer subroutine capable of handling large band matrices. Originally devised by McCormick[16] for treating large distributed elastic systems, the method is based on triangular resolution of the band matrix without interchanges.

The matrix $\mathbf{H}$ is put into upper triangular form, i.e., zeros below the diagonal, by Gaussian elimination, taking the successive pivots along the principal diagonal. The upper triangular matrix is called $\mathbf{U}$. If the successive multipliers are arranged in columns to form the matrix

$$\mathbf{L}=\begin{pmatrix} 1 & & & & & & \\ l_{21} & 1 & & & & 0 & \\ l_{31} & l_{32} & 1 & & & & \\ \cdot & \cdot & 1 & \cdot & & & \\ \cdot & \cdot & \cdot & & \cdot & & \\ \cdot & \cdot & \cdot & & & \cdot & \\ l_{Q_2} & l_{Q_2} & \cdots & & & & 1 \end{pmatrix},$$

where the first column is composed of the multipliers $l_{j1}=-H_{j1}/H_{11}$, $j=2,\ 3\cdots Q$, used to eliminate the first unknown from the last $Q-1$ equations, and so on, the following relation holds:

$$\mathbf{LU}=\mathbf{H}. \tag{29}$$

Hence, we can find the solution χ by solving

$$\mathbf{Lz}=\mathbf{b}, \tag{30a}$$

$$\mathbf{U}\chi=\mathbf{z}, \tag{30b}$$

sequentially by back-substitution. A great computational advantage of the triangular resolution scheme for band matrices is realized as reduced storage requirements and running times compared with conventional matrix inversion routines. This is so because at each stage of elimination only B rows of $\mathbf{H}$ need be contained in the core of the computer, so about $B^2/2$ locations are required for a symmetric matrix. McCormick has made provision for very large ($10^4\times10^4$) matrices by using magnetic tapes to store $\mathbf{H}$ and $\mathbf{b}$ and disk files to store the triangularized matrices. Once the triangular resolution has been effected, the L and U matrices may be used to operate on as many right-hand-side vectors $\mathbf{b}$ as desired. The program is very efficient and execution times are surprisingly low. We feel that this direct method is superior to any of the relaxation techniques.

The solution may be improved iteratively to specified accuracy. This is done by solving Eqs. (30) to a first approximation χ_0. Then a residual vector $\delta\mathbf{b}=\mathbf{b}-\mathbf{b}_0$ is calculated using $\mathbf{b}_0=\mathbf{H}\chi_0$. A correction $\delta\chi$ to χ_0 is calculated using Eqs. (30) with $\mathbf{b}$ replaced by $\delta\mathbf{b}$. This procedure is repeated until $|\delta\chi/\chi|$ is less than a specified number ϵ or until a specified maximum number of iterations have been completed. For the finite-difference equations one iteration is sufficient to obtain an accuracy of one part in 10^7.

Analysis of χ_j

If we multiply Eq. (10a) by ϕ_m^* and integrate with respect to y from $-\infty$ to $+\infty$ we obtain (for $m\leq N$) for $x\leq x_0'$

$$A_m^{(j)}\exp(-i\,|\,k_m\,|\,x)+\bar{A}_m^{(j)}\exp(i\,|\,k_m\,|\,x)$$
$$=\int_{-\infty}^{\infty}\phi_m^*(y)\chi_j(x,y)\,dy$$
$$=f_m^{(j)}(x). \tag{31}$$

A similar equation involving the virtual-channel coefficients $B_m^{(j)}$ and $\bar{B}_m^{(j)}$ may be obtained if $m>N$. The left member of Eq. (31) follows from the orthonormality of ϕ_l. Choosing two different values of x, say x_1 and x_2 in the asymptotic ($x\geq x_0$), gives us two simultaneous linear equations from which to determine $A_m^{(j)}$ and $\bar{A}_m^{(j)}$. We have, dropping the subscript m and superscript j,

$$A\exp(-i\,|\,k\,|\,x_1)+\bar{A}\exp(i\,|\,k\,|\,x_1)=f(x_1), \tag{32a}$$

$$A\exp(-i\,|\,k\,|\,x_2)+\bar{A}\exp(i\,|\,k\,|\,x_2)=f(x_2). \tag{32b}$$

These equations may be solved trivially:

$$A=\frac{[f(x_1)\exp(i\,|\,k\,|\,x_2)-f(x_2)\exp(i\,|\,k\,|\,x_1)]}{\{\exp[-i\,|\,k\,|\,(x_1-x_2)]-\exp[i\,|\,k\,|\,(x_1-x_2)]\}}, \tag{33a}$$

$$\bar{A}=\frac{[f(x_2)\exp(-i\,|\,k\,|\,x_1)-f(x_1)\exp(-i\,|\,k\,|\,x_2)]}{\{\exp[-i\,|\,k\,|\,(x_1-x_2)]-\exp[i\,|\,k\,|\,(x_1-x_2)]\}}. \tag{33b}$$

Clearly, from Eqs. (33)

$$A^*=\bar{A},\ \text{for real}\ f. \tag{34}$$

Repeated evaluations of A and $\bar{A}$ using different pairs of values of $x\geq x_0$ (or $x\leq x_0'$) give agreement to 1% or 2% (depending on the mesh size) for the cases of vibrational excitation treated in Sec. IV below. The integrals $f_m^{(j)}$ are evaluated using the extended Simpson's rule.[17] For selected analytical functions this method yields integrals accurate to one part in 10^8.

IV. APPLICATION OF THE THEORY TO VIBRATIONAL EXCITATIONS

In this section we apply the theory to two collinear models for vibrational excitation of a diatomic molecule

[16] C. McCormick and K. Hebert, "Solution of Linear Equations with Digital Computers," Technical Report, Engineering Division, California Institute of Technology, 1965 (unpublished).

[17] M. Abramowitz and I. Stegun, Natl. Bur. Std. (U.S.) Appl. Math. Ser. 55, 886 (1964).

TABLE I. Transition probabilities as a function of mesh size for the impulsive collision of a free particle with a particle bound in an infinite square well ($E'=2.25$; number of virtuals$=1$; $a=\pi$; $m_A/m_B=1$).

Mesh size	$P_{1\to1}$	$P_{1\to2}$	$P_{1\to1}+P_{1\to2}$	$P_{2\to1}$	$P_{2\to2}$	$P_{2\to1}+P_{2\to2}$
0.1745	0.5468	0.4463	0.9931	0.4602	0.5468	1.0070
0.1571	0.5498	0.4446	0.9944	0.4557	0.5499	1.0056
0.1428	0.5521	0.4433	0.9954	0.4524	0.5522	1.0046
0.1309	0.5538	0.4423	0.9961	0.4500	0.5539	1.0039
0.1208	0.5552	0.4415	0.9967	0.4480	0.5552	1.0032
Extrapolated value	0.5606	0.4387	0.9993	0.4399	0.5607	1.0007

by an atom. We consider the impulsive (hard-sphere) collision of a free particle with a particle bound to a fixed center of force. A schematic diagram of the coordinate system and boundary conditions is shown in Fig. 4. Note that transmission is not allowed in this case, so that it is necessary to solve for only $M\chi_j$'s instead of $2M$.

1. Infinite Square-Well Binding Potential

The Schrödinger equation for this system is simply

$$-\frac{\hbar^2}{2m_A}\frac{\partial^2\psi}{\partial x^2}-\frac{\hbar^2}{2m_B}\frac{\partial^2\psi}{\partial y^2}=E_r\psi, \tag{35}$$

where $x\geq y$ and $0\leq y\leq a$, a being the width of the square well. Making the substitutions $x=(a/\pi)x'$, $y=(a/\pi)y'$ and dividing by $\hbar^2\pi^2/m_Ba^2$, we obtain

$$\{-[2(m_A/m_B)]^{-1}(\partial^2/\partial x'^2)-\tfrac{1}{2}(\partial^2/\partial y'^2)\}\psi=E_r'\psi, \tag{36}$$

where $E_r'=(m_Ba^2/\hbar^2\pi^2)E_r$. The bound states of the well are described by the eigenfunctions

$$\phi_n=(2/\pi)^{1/2}\sin nx', \tag{37}$$

with eigenvalues $\epsilon_n=\frac{1}{2}n^2$. The energy conservation relation is

$$E_r'=\tfrac{1}{2}n^2+(m_B/m_A)(a^2/\pi^2)\tfrac{1}{2}k_n^2 \tag{38}$$

for all n; k_n is the wavenumber of the free particle. Transition probabilities have been obtained for two different total energies and the following parameters: $a=\pi$; $x_0=a$; $m_A/m_B=1.0$. It was found necessary to include only one virtual channel in the state expansion for the range of mesh sizes considered. Adding one or two more virtuals did not change the transition probabilities before the fifth decimal place. Table I lists transition probabilities as a function of the mesh size together with the $e_1{}^m$-extrapolated probabilities,[15] which differ by $\pm.005$ to ±0.01 from values obtained for the finest mesh. For $E_r'=4.75$ units (three open channels) lists of transition probabilities are given in Table II. Again it was sufficient to retain only one virtual in the state expansion.

From Tables I and II we see that the current sum check, i.e.,

$$\sum_{j=1}^{N}P_{i\to j}=1,$$

improves as we decrease the mesh size; also that the sum check for extrapolated values is better than that for the finest mesh. The same is true for the check afforded by the time-reversal requirement $P_{i\to j}=P_{j\to i}$.

2. Parabolic Binding Potential

For the collision of a free hard sphere with a hard-sphere harmonic oscillator we may write the Schrödinger equation as

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial y^2}+\tfrac{1}{2}\kappa(y-y_0)^2\right]\psi=E_r\psi \tag{39}$$

where m is the mass of the free particle, M the mass of the oscillator, κ the force constant, and y_0 the equilibrium position of the oscillator. If we make the changes of variables

$$\xi=(M\omega/\hbar)^{1/2}(y-y_0),$$

$$\xi'=(M\omega/\hbar)^{1/2}x,$$

Eq. (39) becomes

$$[-\tfrac{1}{2}(m/M)^{-1}(\partial^2/\partial\xi'^2)-\tfrac{1}{2}(\partial^2/\partial\xi^2)+\tfrac{1}{2}\xi^2]\psi=E'\psi, \tag{40}$$

where $E'=(\hbar\omega)^{-1}E_r$ and $\kappa=M\omega^2$, ω being the classical frequency of the oscillator. In these units the eigenstates of the oscillator are described by

$$\phi_n=(2^nn!\sqrt{\pi})^{-1/2}H_n(\xi)\exp(-\xi^2/2) \tag{41}$$

and $\epsilon_n=n+\frac{1}{2}$, where H_n is the Hermite polynomial. The energy conservation relation determining k_n, the free-particle wave number, is

$$E_{KE}{}^{(n)}+(n+\tfrac{1}{2})=E'. \tag{42}$$

The $\chi_j(\xi',\xi)$ are determined by solving Eq. (40) with the boundary condition $\chi_j=0$ for $|\xi|\leq a$ and

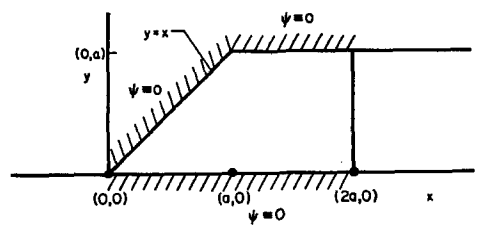

FIG. 4. Schematic of the coordinate system and boundary conditions for the impulsive collision of a free particle with a particle bound to a fixed equilibrium position.

taking a large enough that the χ_j are in fact small compared to their maximum value when $|\xi|>a$. Transition probabilities were determined for several total energies E' using the following set of parameters: $a=10$; ξ_0' (cutoff in the asymptotic region) $=10$; $m/M=\frac{1}{2}$. Table III lists the $e_1{}^m$-extrapolated[15] transition probabilities for $E'=1.75$. In this case there are two open channels and it was sufficient to retain two virtual channels in the state expansion. In Table IV we give the $e_1{}^m$-extrapolated[15] transition probabilities for $E'=2.75$, in which case there were three open and two virtual channels in the state expansion. In general, we find that the current-sum and time-reversal checks improve as the mesh size decreases, the extrapolated values satisfying these requirements better than the finest-mesh values. These results also agree with those of Shuler and Zwanzig[7] to ± 0.02.

TABLE II. Transition probabilities as a function of mesh size for impulsive collision of a free particle with a particle bound in an infinite square well ($E'=4.75$; number of virtuals$=1$; $a=\pi$; $m_A/m_B=1$).

Mesh size	$P_{1\to1}$	$P_{1\to2}$	$P_{1\to3}$	$\sum_{i=1}^{3}P_{1\to i}$
0.1745	0.6126	0.1281	0.2470	0.9877
0.1571	0.6121	0.1304	0.2475	0.9900
0.1428	0.6115	0.1325	0.2477	0.9917
0.1309	0.6108	0.1345	0.2477	0.9930
0.1208	0.6103	0.1362	0.2477	0.9942
Extrapolated value	0.6072	0.1466	0.2477	1.0015
	$P_{2\to1}$	$P_{2\to2}$	$P_{2\to3}$	$\sum_{i=1}^{3}P_{2\to i}$
0.1745	0.1321	0.6069	0.2564	0.9954
0.1571	0.1337	0.6050	0.2576	0.9963
0.1428	0.1353	0.6034	0.2583	0.9970
0.1309	0.1368	0.6019	0.2587	0.9974
0.1208	0.1382	0.6008	0.2588	0.9978
Extrapolated value	0.1473	0.5965	0.2588	1.0026
	$P_{3\to1}$	$P_{3\to2}$	$P_{3\to3}$	$\sum_{i=1}^{3}P_{3\to i}$
0.1745	0.2681	0.2698	0.4796	1.0175
0.1571	0.2645	0.2684	0.4812	1.0141
0.1428	0.2617	0.2673	0.4827	1.0117
0.1309	0.2594	0.2662	0.4841	1.0097
0.1208	0.2575	0.2652	0.4855	1.0082
Extrapolated value	0.2461	0.2529	0.5010[a]	0.9999

[a] This extrapolant is derived by using a more general e^k transformation on the first four values. Inclusion of the fifth value led to some instability. Least-squares fitting yields values of 0.5123 and 0.4985 for second and first degree polynomials, respectively.

Observing that the extrapolated values seem to differ from the finest-mesh values by approximately ± 0.006, we have calculated transition probabilities in the range $E'=1.50$–2.50 (two open and two virtual channels) using the mesh size $h=0.3125$ ($n_w=31$). The transition-probability-versus-total-incident-energy curves (see Fig. 5) agree to ± 0.02 with previously calculated curves,[7] taking into account the extrapolation error and the error in reading Shuler and Zwanzig's curves.

TABLE III. Extrapolated transition probabilities for hard-sphere–harmonic-oscillator collision ($E=1.75$; number of virtuals$=2$; $a=10.0$; $m/M=\frac{1}{2}$).

Final state	0	1
Incident state		
0	0.4941	0.5044
1	0.5084	0.4941

V. SUMMARY AND DISCUSSION

We have presented a quite general method for the quantum-mechanical treatment of the inelastic collision of composite particles. The essential feature of the method consists of forming the total stationary scattering solution describing the collision by taking a linear combination of members of a set of linearly independent functions, each member of the set satisfying the relevant Schrödinger equation in addition to an arbitrary boundary condition specified in the asymptotic region. We have shown that the functions of the linearly independent set may be found using the finite-difference method and that the finite-difference equations can be quickly and accurately solved by the McCormick subroutine[16] because of the band structure of the matrix associated with these equations.

Two examples of collinear impulsive collisions have been treated and in the one case, for which a comparison with previous results is possible, (free-particle–harmonic-oscillator collision) the results are in good agreement.

The success of our method in the treatment of impulsive collisions indicates that it should be useful for general interaction potentials V_I, since the only modification occurs in the diagonal elements of the $\mathbf{H}$ matrix. For long-range interaction potentials the finite-difference equations must be solved over a large interaction region. For problems involving vibrational excitations this may cause no difficulty, since, as we found for the free-particle–harmonic-oscillator collision,

TABLE IV. Extrapolated transition probabilities for hard-sphere–harmonic-oscillator collision ($E=2.75$; number of virtuals$=2$; $a=10.0$; $m/M=\frac{1}{2}$).

Final state	0	1	2
Incident state			
0	0.0014	0.5903	0.3981
1	0.5988	0.1595	0.2414
2	0.4059	0.2480	0.3506

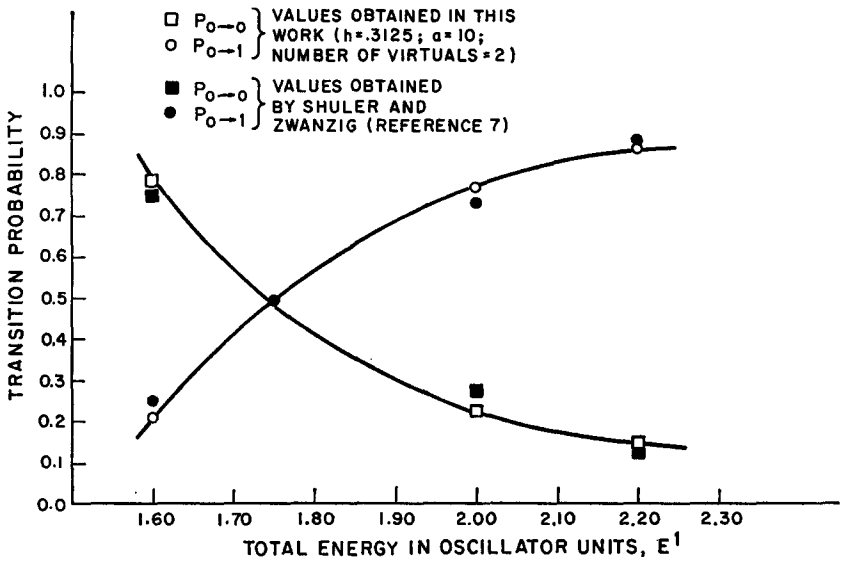

FIG. 5. Transition probability vs total incident energy for the impulsive harmonic-oscillator–free-particle collision.

it seems possible to obtain convergence of transition probabilities using relatively crude meshes. An alternative procedure which may circumvent the problem of large interaction regions is to solve the χ equations using the expansion technique mentioned at the beginning of Sec. III. We are presently applying this technique to the free-particle–harmonic-oscillator collision with a Lennard-Jones 6–12 interaction potential.

It does not appear practical to use the finite-difference method to solve directly the χ equations for three-dimensional collisions, since the number of equations increases as $[(a/h)-1]^n$, where a is the range of each variable, h the mesh size, and n is the number of variables. Thus, for a three-dimensional two-particle problem (six variables) one would be required to solve a very large number of simultaneous equations even for a very crude mesh. This is a formidable task even if the matrix is banded. However, it may be possible to solve the problem indirectly by using a state expansion of the form $\Psi=\sum_j f_j\phi_j$, where ϕ_j are the bound-state eigenfunctions of the composite particles and f_j are arbitrary functions of the relative coordinate between the centers of mass. For instance, suppose we are interested in the collision of two diatomic molecules. Following Takayanagi's[1a] formal treatment, we expand the total scattering wavefunction Ψ as

$$\Psi=\sum_{j\nu\lambda} f(j,\nu,\lambda\mid k_\lambda,R)R^{-1}$$
$$\times\Phi(j,\nu,\lambda\mid\theta,\phi,r_1,\theta_1,\phi_1,\chi_1,r_2,\theta_2,\phi_2,\chi_2), \quad (43)$$

where R is the distance between the centers of mass of the molecules and Φ are the vibrational–rotational eigenfunctions of the free molecules, characterized by quantum numbers j, ν, and λ. We obtain an infinite set of coupled equations for the f's by making use of the orthonormality of the various factors in Ψ. These equations may be expressed as

$$\frac{\hbar^2}{2M}\left\{\frac{d^2}{dR^2}-\frac{j(j+1)}{R^2}+k_\lambda^2\right\}f(j',\nu',\lambda'\mid k_{\lambda'},R)$$
$$=\sum_{j\nu\lambda} V_{j'\nu'\lambda'j\nu\lambda}f(j,\nu,\lambda\mid k_\lambda R). \quad (44)$$

Our approach to the solution of this set of coupled equations is as follows. Having truncated the expansions in j, ν, and λ, we solve the finite-difference equations to obtain *sets* of f's corresponding to independent boundary conditions specified in the asymptotic region. Then we take an appropriate linear combination of these sets to satisfy the correct asymptotic condition on the total wavefunction Ψ. Although the finite-difference matrix is symmetric, it is not banded in this case. However, the total number of equations is given by the product of the number of states retained in the truncated expansion Eq. (44) and the number of mesh points, there being only one variable R. If we can tolerate a small number of both mesh points and expansion states, it may be relatively easy to solve the coupled finite-difference equations.

An attractive feature of our method is its applicability to exchange reactions. We shall present results for some model exchange reactions in a future paper.[10]

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